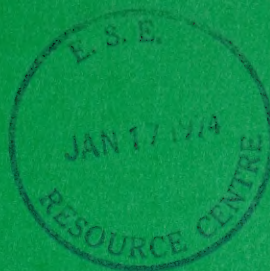


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METHODS FOR THE REMOVAL
OF SULPHUR FROM COAL

by

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Engineering Division
Technology Development Branch
Air Pollution Control Directorate

Report EPS 3-AP-73-3

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ABSTRACT

A review is given of methods which are in use, or which are undergoing development, for the removal of sulphur from coal. The methods in widespread use are concerned with the removal of discrete particles containing inorganically bound sulphur (essentially FeS_2) from the coal matrix. For high-sulphur coals, such methods provide only a partial solution to the problem of the control of sulphur dioxide emission from coal combustion. No commercial techniques are available for the removal of organically bound sulphur from coal. However, methods under development are described which can accomplish virtually complete inorganic, and some inorganic, sulphur removal from coal, and which could provide a viable alternative to the removal of sulphur dioxide from flue gases for emission control.

RÉSUMÉ

Les auteurs présentent une revue des méthodes qui sont en usage, ou qui sont sous développement, pour enlever le soufre du charbon. Les méthodes qui sont le plus en usage ont à faire avec l'enlevage de particules distinctes contenant le soufre relié sous forme inorganique (essentiellement FeS_2) de la matrice du charbon. Aucune techniques commerciales sont disponibles pour l'enlevage du soufre relié sous forme organique du charbon. Pour les charbons hauts en soufre, de telles méthodes ne donnent qu'une solution partielle au problème du contrôle des émissions du dioxyde de soufre qui se dégagent durant la combustion du charbon. Cependant, des méthodes sous développement sont décrites qui peuvent accomplir l'enlèvement presque total sous forme inorganique et l'enlèvement partiel du soufre sous forme organique du charbon, et qui pourraient présenter une alternative pour l'enlèvement du dioxyde de soufre des gaz de combustion pour le contrôle des émissions.

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
RESUMÉ	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	vii
LIST OF TABLES	viii
1. INTRODUCTION	1
2. OCCURRENCE OF SULPHUR IN COAL	4
3. GRINDING	4
4. PHYSICAL SEPARATION METHODS	9
4.1 WET METHODS	10
4.1.1 Dense Medium Liquids	10
4.1.2 Separators	12
4.1.3 Flotation	19
4.1.4 Spherical Agglomeration	25
4.2 DRY SEPARATION METHODS	28
5. CHEMICAL SEPARATION METHODS	33
5.1 SOLVENT-REFINED COAL	33
5.2 FERRIC-ION LEACHING	37
5.3 ORGANIC-SOLVENT LEACHING	39
5.4 ALKALINE LEACHING	41
6. OTHER METHODS	43
7. SUMMARY	45
REFERENCES	47



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LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Relationship between Clean Coal Yield and Specific Gravity of Separation, using a Washing Table.	14
2.	Effect of Impeller Speed on the Flotation Rate of Coal	24
3.	Effect of Reagent Additions on the Flotation Rate of Coal	24
4.	Schematic of the Pittsburgh and Midway Solvent-Refined-Coal Process	34
5.	Pyritic Sulphur Removal from Coal by Ferric-Ion Leaching	40
6.	Organic Sulphur Removal from Coal	42

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	EPA Performance Standards for Fossil-Fired Steam Generators	2
2.	Pyritic Sulphur Reduction at 1.6 Specific Gravity, as Related to Nominal Top-Size, for Various United States Coals	6
3.	The Effect of Coal Size on Sulphur Reduction of Illinois Coals	7
4.	The Use of Industrial Processes for the Cleaning of Coal (U.S.A. 1965)	9
5.	Estimated Costs of Desulphurizing Coal by Heavy-Medium Separation	11
6.	Analysis of the Product from the Tables from the Classifier-Washing Table Circuit	15
7.	Predicted Results of Cleaning in a Dense Medium Cyclone (Allegheny County, Pittsburgh Coal)	16
8.	The Cleaning of Three Size-Fractions of Coal with a Humphrey's Spiral	18
9.	Reagent Cost for Ash Removal from Coal by Flotation	21
10.	Percentage Ash and Sulphur Removal by Flotation and by Hydrocycloning as a Function of Particle Size	22
11.	Agglomeration and De-Watering of a 28 x 0-Mesh Western Canada Coal	26
12.	Influence of Various Oils on the Beneficiation of Coal	27

<u>Table</u>		<u>Page</u>
13.	The Dry Removal of Pyrite from Closely Sized Fractions of Pittsburgh Coal by Centrifugal Action	29
14.	The Magnetic Susceptibilities of Some Iron Compounds and the 'Apparent' Susceptibility of Pyrite if One Per Cent of the Compound were Present in the Pyrite	32
15.	The Removal of Pyritic Sulphur from Coal by Six One-Hour Leaches with One-Molar FeCl_3 Solutions	38

1. INTRODUCTION

The present energy needs of the world are supplied mainly by the combustion of oil, natural gas, and coal, with relatively minor contributions provided by nuclear and hydroelectric sources (1). However, the consumption of energy has for some time grown exponentially, and if, as forecast, this trend continues in the future very heavy demands will be placed on fossil-fuel supplies (2-4). As reserves of fossil fuels are finite, concern is currently being expressed over the continued availability of oil and natural gas as cheap and abundant fuels (1,5,6). This situation is particularly grave in the United States where the domestic production of oil and natural gas is no longer adequate to meet demands for these fuels. Thus it is forecast that, from a self-sufficiency in oil supplies in 1968, the United States will need to import forty-six per cent of its oil requirements by 1980 (7). A similar situation exists for natural gas. It is expected that domestic gas production will peak in the mid-1970's, to be followed later by an increasing gap between supply and demand which will place a very heavy reliance on imports and on supplemental gas supplies (8,9). In Canada, at the 1970 rate of production, the currently known gas reserves in producing areas will be exhausted in just under thirty years and constraints are now being placed on the amount of gas available for export (10). However, in Canada and elsewhere, reserves of all ranks of coal are very large and, on a global basis, coal represents about ninety per cent of the world's inventory of fossil fuels (11). It is apparent, therefore, that as oil and natural gas become scarcer and more expensive, coal will be required to play an important role as a primary energy resource (12,13), both for direct combustion and as a source for synthetic natural gas and oil (14,15).

Unfortunately coal, unlike natural gas, is not a clean fuel and it contains, among other impurities, significant quantities

of sulphur compounds. During combustion these are oxidized and released to the atmosphere, mainly in the form of sulphur dioxide. The adverse effects of sulphur dioxide on health, plant growth and constructional materials are well recognized (16-22) and, emission standards are being established in various countries to limit the amount of sulphur dioxide, and other pollutants, that may be discharged from a given industrial process (23). For example, the Environmental Protection Agency (EPA) in the United States has recently established national emission standards for new and modified fossil-fueled steam generators (24), which apply to units with a capacity of 250 MBtu ($\sim$ 22MW)/hr. or larger (Table 1).

TABLE 1

EPA PERFORMANCE STANDARDS FOR FOSSIL-FIRED STEAM GENERATORS

Fuel Type	Standards (Lbs Per Million Btu)		
	Particulates	Sulphur Oxides	Nitrogen Oxides
Solid	0.10	1.2	0.70
Liquid	0.10	0.80	0.30
Gaseous	-	-	0.20

For a coal-fired boiler these standards may be met by the combustion of coal containing not greater than 0.8 per cent sulphur (based upon 13,300 Btu/lb of coal).

At present, the main use of coal is for the generation of electrical power. On the assumption that no radical technological innovations in power generation are likely to arise in the near future, it is expected that in the United States coal will maintain its dominant position in this field for the next twenty

to thirty years and that the annual consumption of coal for power generation will double between 1970 and 1990 (25,26). Quite often large quantities of low-sulphur coal are not available close to industrialized areas. To meet sulphur dioxide emission standards, this situation has led to the conversion of some coal-burning power-plants to natural gas or to expensive low-sulphur oil. An alternative approach adopted in some cases has been to change temporarily to the combustion of low-sulphur coal during atmospheric conditions unfavourable to the dispersion of sulphur dioxide from tall stacks (27). Western Canadian coals are usually low in sulphur (typically around 0.6 per cent) and the only high-sulphur coals produced in Canada are from the Atlantic provinces (28,29). However, considerable quantities of high-sulphur coal are burned in Ontario (imported from the United States) and the coal used by Ontario Hydro in 1970 contained between 2 to 2.6 per cent sulphur (30). The coal used by electrical utility companies in the United States in 1969 ranged in sulphur content from 0.4 to 6 per cent and had an average sulphur content of 2.58 per cent (31).

In principle, the amount of sulphur dioxide emitted from the combustion of coal can be limited in three ways.

The removal of all, or part, of the sulphur-containing compounds prior to combustion.
Trapping sulphur during combustion by some process such as fluidized-bed combustion (32-34).

The removal of sulphur dioxide from stack gases, by physical or chemical means, before their discharge to the atmosphere (35-38).

This report is concerned with the first approach and the other two methods will be considered in subsequent publications.

2. OCCURRENCE OF SULPHUR IN COAL

Sulphur occurs in coal in organic and inorganic compounds. The inorganic sulphur is present in freshly mined coal mainly as iron disulphides (FeS_2) - pyrite, and to a lesser extent its orthorhombic modification, marcasite - together with small amounts of various metal sulphates which are not of major significance. However, it should be noted that the amount of sulphate sulphur in coal can increase rapidly on weathering due to the oxidation of the iron disulphides by bacterial and other action (39). Pyrite is physically present in coal both as discrete particles, ranging in size from small grains (two microns or less) disseminated throughout the coal structure to nodules large enough to be hand picked (40-44), and also as hair-like veins and lenses extending considerable distances in the coal bed (40). For most coals, however, the pyrite occurs in the size range between 20 and 200 microns (41).

The organic sulphur in coal is chemically bound in the coal matrix as aliphatic and aromatic sulphur compounds of differing stabilities (45), and cannot be separated from the coal without the breaking of chemical bonds. The total concentration of sulphur in coals varies from a few tenths of one per cent to as much as nine per cent (40,42) and as a rough guide may be taken as being equally distributed between the organic and the inorganic forms (40,42, 46-48). However, the ratio of inorganic:organic sulphur is not constant, even for a given coal (49), and the pyritic sulphur content of different coal deposits may range from 5 to 90 per cent of the total sulphur content of the coal (40).

3. GRINDING

As a precursor to physical separation processes for the removal of pyrite from coal, the coal must first be ground to liberate the pyrite. The liberation of most of the ash minerals

(including pyrite) requires grinding to at least minus 200 mesh (14,30,50). Grinding to minus 400-mesh would liberate additional very small pyrite particles but this can seldom be justified economically. The coal used in thermal power stations is normally ground to minus 200 mesh (p.c. grind) to give a pulverized coal in which not all of the finely disseminated pyrite is liberated.

Stage crushing has been examined (51) as a potential method for the selective reduction of the pyrite content of coals from five different coal beds in the Appalachian region, using a sink-and-float test method. For some of the coals the degree of pyrite removal increased as a function of the fineness of grinding, but no general trends were common to all the samples. A more detailed study has been made along similar lines (52) of coals from twenty-two sources in the United States, using stage crushing from 1/8-inch to minus 200 mesh. A specific gravity separation method was again employed and it was assumed that all the sulphur removed from the float fraction was associated with pyrite. Approximately one-half of the coals showed no significant reduction in pyritic sulphur content with reduction in particle size, and some representative data are given in Table 2. Similar results were obtained in an investigation (53) of the removal of pyritic sulphur from forty coal samples taken from thirty-five mines in Illinois. These coals had a total sulphur content ranging from three to five per cent and contained an average of 2.36 per cent pyritic and 1.77 per cent organic sulphur. Separations were conducted by the float-and-sink method at specific gravities ranging from 1.23 to 1.60. The average results from the forty samples are given in Table 3.

TABLE 2

PYRITIC SULPHUR REDUCTION AT 1.6 SPECIFIC GRAVITY, AS RELATED TO
NOMINAL TOP-SIZE, FOR VARIOUS UNITED STATES COALS

Coal Source	Pyritic Sulphur Content of Coal (wt %)	Percentage Reduction at 1.6 Specific Gravity			
		3/8" x 100M	14M x 0	30M x 0	p.c. Grind
Clairbourne, Tennessee	0.39	51.9	51.9	53.8	53.8
Marion, Tennessee	0.42	90.5	95.2	81.0	90.5
Moffat, Colorado	0.09	0.0	0.0	33.3	33.3
Mahaska, Iowa	3.49	50.8	58.2	66.0	77.9
Chelsea, Oklahoma	0.95	17.7	27.4	47.4	83.2
Chelsea, Oklahoma	0.20	33.3	66.6	20.0	30.0
Franklin, Arkansas	2.92	14.7	20.8	36.3	60.3
Haskell, Oklahoma	0.28	53.3	75.0	21.4	21.4
Marion, Tennessee	0.25	41.2	50.0	44.0	44.0

TABLE 3
THE EFFECT OF COAL SIZE ON SULPHUR REDUCTION OF
ILLINOIS COALS

Recovery (%)	Total Sulphur in Recovered Coal (%)			Pyritic Sulphur in Recovered Coal (%)		
	1½" x 0	3/8"x14M	14Mx100M	1½" x 0	3/8"x14M	14Mx100M
40	2.35	2.33	2.24	0.55	0.52	0.39
50	2.43	2.40	2.33	0.62	0.58	0.48
60	2.54	2.48	2.46	0.73	0.68	0.61
70	2.69	2.60	2.60	0.89	0.81	0.78
80	2.87	2.75	2.78	1.09	0.97	0.99

The cleaned coal fractions usually had a lower pyrite content when crushed to finer sizes but the overall improvement in sulphur removal with decrease in coal size was considered insufficient to make fine grinding an attractive method for the removal of sulphur from most of these coals. For a 40 per cent recovery, which would be unacceptable in mining practice, an average of 83.6 per cent of the pyritic sulphur was removed from coal ground to the size range of 14 to 100 mesh.

The distribution of pyritic sulphur in a Cape Breton coal has been studied (28) as a function of coal size, using heavy medium separation (specific gravity of 1.6). The results indicate that if a suitable physical separation process were available, grinding to 325 mesh would permit 70 per cent of the pyritic sulphur to be removed.

The reject fraction from coal cleaning has a relatively high ash and sulphur content and feasibility studies have been made (54) on methods to recover the calorific value and the sulphur content of this fraction to partly offset the cost of coal cleaning. The combustion of a reject fraction with a sulphur:carbon weight ratio of 1.8 will give a flue gas containing about six per cent sulphur dioxide. This concentration is sufficiently high for direct conversion of the sulphur dioxide to sulphuric acid by the conventional catalytic oxidation process (35). However, for reject fractions with a sulphur:carbon weight ratio below unity, the sulphur dioxide in the flue gas (concentration <4%) will require an additional concentration step prior to the production of sulphuric acid or of a sulphur-containing product.

In general, the degree of pyrite liberation on grinding is dependent not only on the final product size but also on the source of the coal and the physical distribution of the pyrite. The amount of inorganic (pyritic) sulphur liberated from many coals may be increased by finer grinding (54), but the organic sulphur content, due to its intimate association with the coal structure, will be virtually unaffected by grinding and is not amenable to reduction by conventional mechanical cleaning.

The separation of the liberated pyrite from coal may be accomplished by a variety of physical and chemical methods which depend on differences in the properties of the two solids. These methods will now be considered.

4. PHYSICAL SEPARATION METHODS

Techniques for the physical separation of coal from ash minerals may be conveniently divided into wet and dry methods. With the exception of flotation, the methods (55) used industrially for the cleaning of coal (Table 4) depend upon the difference in density between coal ($d = 1.3 \text{ g/cm}^3$) and its mineral impurities (pyrite, $d = 5.0 \text{ g/cm}^3$; shale, $d = 2.0 \text{ to } 2.7 \text{ g/cm}^3$).

TABLE 4

THE USE OF INDUSTRIAL PROCESSES FOR THE
CLEANING OF COAL (U.S.A. 1965)

Process	Per Cent Used
Jig	46
Dense Medium	29
Washing Table	13
Pneumatic	8
Flotation	2
Others	3

These methods are suitable only for the removal of inorganic constituents from coal, and do not affect its organic sulphur content.

4.1 WET METHODS

4.1.1 Dense Medium Liquids

Dense medium cleaning of coal is obtained when pulverized coal is immersed in a liquid whose density is intermediate between that of coal and its impurities. The lower density coal fraction is collected at the surface of the liquid and is skimmed off, while the denser ash is collected at the bottom as a reject. Various organic liquids, such as carbon tetrachloride and acetylene tetrabromide, are potentially useful for the cleaning of coal by heavy-medium separation techniques. However, apart from their use in float-and-sink separators for quality control, organic liquids are not used commercially (56) because of their high initial cost, their toxicity, and the loss of the liquid by absorption in the coal. Dense medium liquids in common practice are obtained using calcium chloride solutions to give liquids of specific gravity ranging from 1.4 to 1.6, as in the Belknap Chloride Process (56), or aqueous suspensions of sand to give specific gravities ranging from 1.5 to 1.7, as in the Chance Process. More recently (57) suspensions of magnetite and ferrosilicon have been used to obtain dense medium liquids of specific gravities ranging from 1.25 to 3.40. The recovery of these suspensions from clean coal is readily achieved by magnetic separation.

Zimmerman (58) has shown, in float-and-sink tests, that the reduction of the pyritic sulphur content of coal is related to the specific gravity of the dense medium liquid (Table 5).

TABLE 5
ESTIMATED COSTS OF DESULPHURIZING COAL BY
HEAVY-MEDIUM SEPARATION

Coal Source Coal Size Specific Gravity of Separation	Illinois No. 6 3½-in. x 0			Ohio No. 8 7-in. x 0		
	1.60	1.45	1.35	1.60	1.45	1.35
Costs per Million Btu (cents)	14.7	15.5	18.3	13.5	14.8	17.2
Coal Recovery (%)	90.0	84.0	68.5	85.0	74.0	60.0
Initial Total Sulphur (%)	2.93	2.93	2.93	3.55	3.55	3.55
Final Total Sulphur (%)	2.43	2.32	2.20	2.62	2.25	1.94
Organic Sulphur (%)	1.85	1.85	1.85	1.50	1.50	1.50
Initial Pyritic Sulphur (%)	1.08	1.08	1.08	2.05	2.05	2.05
Final Pyritic Sulphur (%)	0.58	0.47	0.35	1.12	0.75	0.44
Pyritic Sulphur Reduction (%)	46.2	56.4	67.6	45.4	63.4	78.5
Coal Btu Value/lb	11,900	12,000	12,200	13,000	13,300	13,600

The pyritic sulphur reduction for both coals is greatest for separations at a specific gravity of 1.35 but high costs arise at this specific gravity due to the low yields of clean coal. The author suggests that such yield losses, as shown by float-and-sink analyses, will hold true until improved schemes of separating pyrite from coal are developed.

Hoffman and Yeager (59) have examined the economic factors associated with the physical desulphurization of coal to one per cent total sulphur content. Thirty physically desulphurized United States coal-source/user combinations were analysed and

the study was restricted to coal deposits in which the organic sulphur content of the ROM coal was less than one per cent. The demand for coal in 1970 for stationary sources in the Eastern United States was 380 million tons. The estimated production of coal containing one per cent sulphur was 60 million tons. Sulphur emission controls were therefore needed for 320 million tons of coal. The physical cleaning procedures considered were designed to remove the pyritic sulphur which comprised from 40 to 80 per cent of the total sulphur content of the coals. The physical desulphurization was done in the coal-size range of 1/4 inch to 3/8 inch, which was considered the minimum practical size to prevent dusting prior to shipment. The cleaning conditions were crushing to a 3/8 inch top-size, heavy medium separation at a 1.6 specific gravity, and approximately 90 per cent Btu recovery. About 46 million tons of the current annual United States coal production (which represents 15 per cent of low-sulphur coal needs) was estimated as cleanable to one per cent total sulphur. The study indicated that the production, transportation, and utilization of coal physically cleaned to this sulphur level can produce a net cost to the user ranging from 9 cents/ million Btu to a saving of 1 cent/ million Btu and that physically cleaned coal may be economically attractive for the control of sulphur dioxide emissions.

4.1.2 Separators

Mechanical separators that are used industrially for coal cleaning include the jig (60), the washing table (57,61,62), the hydrocyclone (44,63), the basket separator (42,64), and the Humphrey's spiral (65).

4.1.2.1 Jigs

The jig is a separator in which a bed of solid particles, supported on a porous plate, is stratified by a pulsating fluid flow. The density of the suspended solids increases towards the bottom of the jig where the rejects are removed. The bed may be separated at any particular density to give a product of

the desired quality. Coal washing by jigging is used more than any other cleaning method (Table 4). Jigs have a capacity of up to 700 tons per hour of feed coal and can treat sizes as coarse as eight inches. They are widely used for the removal of ash-forming constituents from coal and can also effectively remove pyrite particles coarser than one millimeter (42). Jigs are easy and economical to operate, but their ability to produce a high-quality low-sulphur product, combined with a high recovery, is limited, and is not as good as that of dense medium devices (60).

4.1.2.2 Washing Tables

The use of washing tables to clean coal is well established (57,61,62). Tables can clean coal at a rate of 15 tons per hour in the size range $1/2$ inch x 0, and 7.5 tons per hour for coal of minus $1/8$ -inch. In general, as the top-size of the feed is reduced the capacity of the table decreases. Geer (66) has found that washing tables are approximately 95 per cent efficient in yield of clean coal at a specific gravity separation of 1.5.

Terchik (67) has investigated the possibility of increasing the efficiency of washing tables at low specific gravity for the removal of sulphur from coal through the use of a combined hydraulic classifier/washing table circuit. A Pittsburgh seam coal containing 2.01 per cent sulphur was used in this study. It was initially ground to minus $1/4$ -inch and separations were made with individual washing tables on seven fractions from the classifier, in the size range of $1/4$ inch to 28 mesh. Overall washing table performance was assessed by dividing the product of each table into seven zones. These zones represented separation at different specific gravities. Three zones for each table were above a specific gravity of 1.52 and were rejected. The results of a composite analysis of the remaining four zones are given in Table 6 and indicate that the difference between the actual and the theoretical sulphur content is small but that there is a substantial loss of efficiency as the specific gravity is lowered. The relationship between the clean-coal yield and the specific gravity of separation obtained by tabling the classified feed is shown in Figure 1.

TABLE 6
ANALYSIS OF THE PRODUCT FROM THE TABLES
FROM THE CLASSIFIER - WASHING TABLE CIRCUIT

Clean Product	Separating Gravity	Yield, Per Cent			Sulphur, Per Cent	
		Theoretical	Actual	Difference	Theoretical	Actual
Product A (Zones 1,2,3,4)	1.52	93.0	79.3	13.7	1.54	1.50
Product B (Zones 1,2,3)	1.48	91.9	75.5	16.4	1.51	1.49
Product C (Zones 1,2)	1.43	89.8	69.3	20.5	1.47	1.46
Product D (Zone 1)	1.37	84.4	60.7	23.7	1.39	1.43

4.1.2.3 Dense Medium Cyclones

The application of the dense medium cyclone to coal cleaning began in Europe in the mid-forties and several commercial plants have more recently begun operation in North America. The coal to be cleaned is usually in the size-range of 3/8 inch to 32 mesh, and cyclone capacities of up to 75 tons per hour are available (68). Magnetite is used for the heavy medium preparation (57,68). The dense medium cyclone has the best capability among commercial coal-cleaning methods for effecting a 'sharp' separation, at a given specific gravity, between coal and its impurities. However, cyclones are more expensive to build and to operate than other coal-cleaning techniques and for many coals do not offer

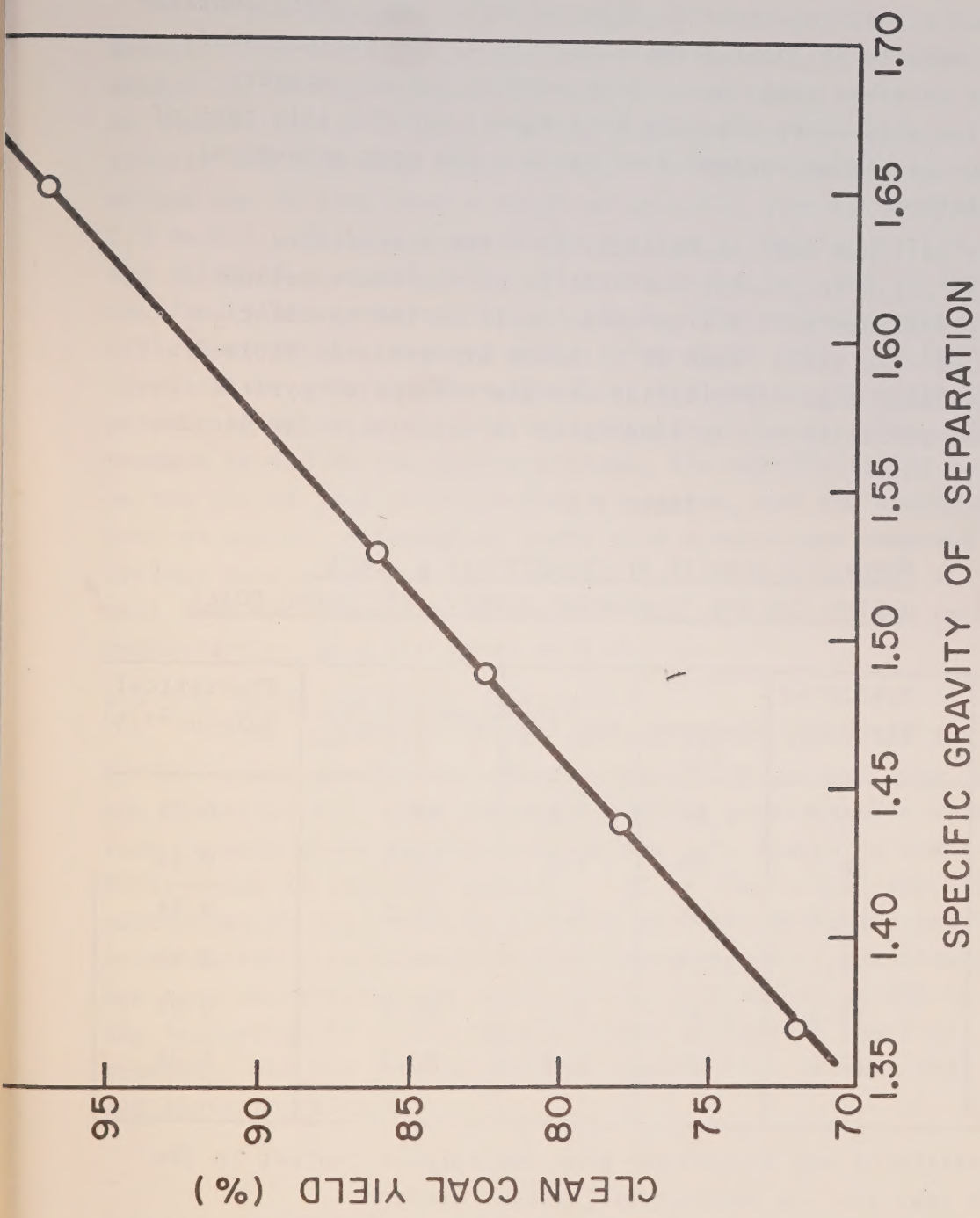


Fig. 1. RELATIONSHIP BETWEEN CLEAN COAL YIELD AND SPECIFIC GRAVITY OF SEPARATION, USING A WASHING TABLE

significantly improved recovery efficiencies. For coals containing large amounts of 'near gravity' material, the sharpness of separation possible with the cyclone permits higher recovery efficiencies than other cleaning techniques, and for this type of coal the dense medium cyclone does provide the most economical cleaning method.

Geer (67) has used washability data for twenty-five Appalachian coals to predict the ability of the dense medium cyclone to separate pyrite from these coals at low specific gravities (1.3 to 1.4). Some of his data are given in Table 7 which shows that high efficiencies for the removal of pyritic sulphur are possible, but in some cases at relatively low yields.

TABLE 7

PREDICTED RESULTS OF CLEANING IN A DENSE
MEDIUM CYCLONE (ALLEGHENY COUNTY, PITTSBURG COAL)

Specific Gravity	Predicted Yield (%)	Sulphur (%)	Ash (%)	Efficiency* (%)	Theoretical Sulphur** (%)
1.30	59.0	1.04	3.1	89.2	0.98
1.32	66.0	1.10	3.5	93.3	0.98
1.34	77.8	1.16	3.8	95.7	0.98
1.36	82.1	1.20	4.1	97.2	0.98
1.38	85.2	1.23	4.2	97.8	0.98
1.40	87.6	1.25	4.4	98.5	1.26

* The efficiency was determined from the sulphur content in the recovered coal and the theoretical sulphur content.

** The theoretical sulphur content was determined by float-and-sink experiments.

4.1.2.4 Compound Water Cyclone

The compound water cyclone was developed at the Mines Branch, Department of Energy, Mines and Resources, Ottawa as an economical method to clean friable Western Canadian coals (69,70). An aqueous slurry of particles of different sizes and specific gravity are separated under hindered settling conditions, and the method may be used over a range of specific gravity cut-points from 1.3 to 2.5. The capacity of the cyclone is related to its diameter and units of up to 36 inches diameter (capacity, 260 to 290 short tons/hour) are commercially available. The overall separation efficiency may be improved using a two-stage unit. In this approach the overflow from the first cyclone is the clean coal product which is de-watered by conventional means. The underflow product is fed to the second cyclone, its overflow being returned to the slurry tank as a middlings fraction, and its underflow being sent to waste. Pilot-plant tests with a two-stage compound water cyclone gave a sulphur and ash reduction for a 3/8 inch x 0 slack coal from West Virginia of about 20 per cent and 25 per cent respectively, at a cut point of 1.68.

4.1.2.5 Other Hydraulic Devices

The Humphrey's spiral and the basket separator are both devices which may be used for the separation of coal from its ash constituents. The Humphrey's spiral consists of a multi-turn conduit which separates materials into fractions based upon differences in specific gravity. It is widely used for the concentration and recovery of heavy minerals but has received only limited attention for the cleaning of coal. Deurbrouck (65) has made an introductory study of the application of the spiral to the separation of pyrite from a Middle Kittanning Bed coal. The recovery, and the pyritic sulphur removal, for various size ranges are shown in Table 8.

TABLE 8

THE CLEANING OF THREE SIZE-FRACTIONS OF
COAL WITH A HUMPHREY'S SPIRAL

Mesh Size	Pyritic Sulphur Content (%)		Recovery (%)	Pyritic Sulphur Reduction(%)
	Feed Coal	Clean Coal		
35 x 200	1.85	0.29	88.3	84.4
35 x 0	1.94	0.86	90.7	55.7
200 x 0	2.07	1.71	94.7	17.4

The spiral was most effective for the separation of pyrite from the 35 by 200 mesh sample, for which the clean coal contained only 0.29 per cent sulphur at a recovery of 88.3 per cent. The efficiency of the Humphrey's spiral for cleaning coal ground to minus 35 mesh was slightly less than that of a conventional washing table, but the higher capacity and lower operating cost of the spiral should offset the small difference in their cleaning ability.

The basket separator is undergoing development in Germany (42) and consists essentially of a basket-stirrer unit which is rotated in an outer cylindrical vessel. An aqueous slurry of coal enters the top of the separator and, under the action of centrifugal and flow forces, heavy material collects at the inner wall of the basket. The lighter material is maintained in the aqueous pulp which is discharged for additional sorting. The contents of the basket are then dislodged by jets of water and rejected through a tailings pipe. Separations are made with a number of units in series which are automatically controlled. The throughput of a given unit depends upon the slurry density and the test units had a capacity of 13.5 tons per hour for a slurry containing

50 weight per cent solids.

Pilot-plant measurements were made with five Ruhr coals using a four-stage basket separator. The coals were ground to minus 16 mesh and the separation gave a 40 to 60 per cent reduction in the total sulphur content and a 20 to 40 per cent reduction in the ash content of the coals. The greatest sulphur removal was found for coal in the size range of 20 to 100 microns.

4.1.3 Flotation

The froth-flotation process is widely used in the mineral industry to separate valuable minerals from gangue materials and extensive research has been conducted to obtain an understanding of the physico-chemical basis of the technique (71-73). Froth flotation is also used commercially to a limited extent for the cleaning of coal (Table 4), but relatively little is known about the underlying mechanisms involved in coal flotation (74). Although coal particles as coarse as 3/16 inch may be floated, it is generally considered uneconomical to use flotation separation for coals coarser than about minus 28-mesh, because these sizes may be treated more cheaply by conventional specific-gravity cleaning methods (75).

The need for fine grinding to liberate pyrite from coal makes froth flotation an attractive coal-cleaning technique; the method depending primarily on the surface properties, and not on the specific gravity, of the particles. However, the floatability of pyrite associated with coal has been reported to be much greater than that of pyrite from inorganic mineral deposits. Depressants, such as lime and sodium cyanide, used for pyrite suppression in mineral-separation processes do not give anticipated results in coal cleaning (41,76). This behaviour has been attributed to the presence of an organic coating on the surface of the 'coal pyrite' which shields the surface of the pyrite from the depressant (77). It has been reported recently (78)

(quebracho extract) was used to keep the clean coal in the tailings for product recovery. The recovery was 60 to 67 per cent with the pyrite content of the coal reduced from 1.75 to 0.27 per cent.

Miller et al. (81) have made a study of the mechanism involved in the froth-flotation recovery of fine coal. The authors report that the recovery rate increases with particle size reduction from 25 mesh to 100 mesh and then remained effectively constant for further size reduction to 325 mesh. They also discuss the problem related to fine-particle cleaning and suggest a combined flotation-hydrocyclone technique for the removal of pyrite from coal. The effectiveness of each technique for different particle sizes is given in Table 10.

TABLE 10
PERCENTAGE ASH AND SULPHUR REMOVAL BY
FLOTATION AND BY HYDROCYCLONING AS A
FUNCTION OF PARTICLE SIZE

Particle Size (Mesh)	Ash Removal (%)		Sulphur Removal (%)	
	Flotation	Hydrocyclone	Flotation	Hydrocyclone
28 - 100	50-60	60-65	50-60	70-80
100 - 200	40-45	40-45	30-40	60-70
200 - 325	40-45	15-18	25-30	35-40
325 - 0	50-55	0-5	20-25	8-10

The percentage removal of sulphur by flotation in the coarser sizes is less than by hydrocyclone separation and it decreases for both methods as the particle size is decreased. Because froth flotation effectively rejects particles that do not contain surface

carbon, this method is better than hydrocyclone separation for the removal of ash material as fine as minus 325 mesh. The authors point out that hydrocyclone performance is affected primarily by the specific gravity and the size of the particles, whereas coal flotation depends on the particle mass and the coal surface available for bubble attachment.

Mackenzie and Matheson (83) have made a study of the effects of particle size, reagent additions, and cell turbulence on the flotation rate of coal. Their work was concerned with bubble encounter and adhesion, and with the kinetics of coal flotation. The relationship between flotation rate and particle diameter with variations in impeller speed and collector concentration is shown in Figures 2 and 3. It is evident from these results that the maximum flotation rate occurs at a particle diameter of approximately 100 microns (150 mesh) for all impeller speeds and collector concentrations. This size is in general agreement with that found by Miller et al. (81) who reported optimum flotation recovery for particles of approximately 150 microns (100 mesh).

Sun and Savage (84) have developed a multi-stage process for the recovery of coal, clays, and pyrite from coal wastes by fine grinding and flotation. A xanthate collector was selected for the pyrite and a pine oil collector-frother for the coal. The optimum pH for coal flotation was found to be 8.5 and for pyrite flotation 5.0. The coal waste initially contained 10 per cent sulphur and 30 per cent carbonaceous material. The separation process gave a coal product containing four per cent sulphur and ten per cent ash with an 89 per cent yield. The pyrite product contained about 84 per cent FeS_2 and one per cent carbonaceous material.

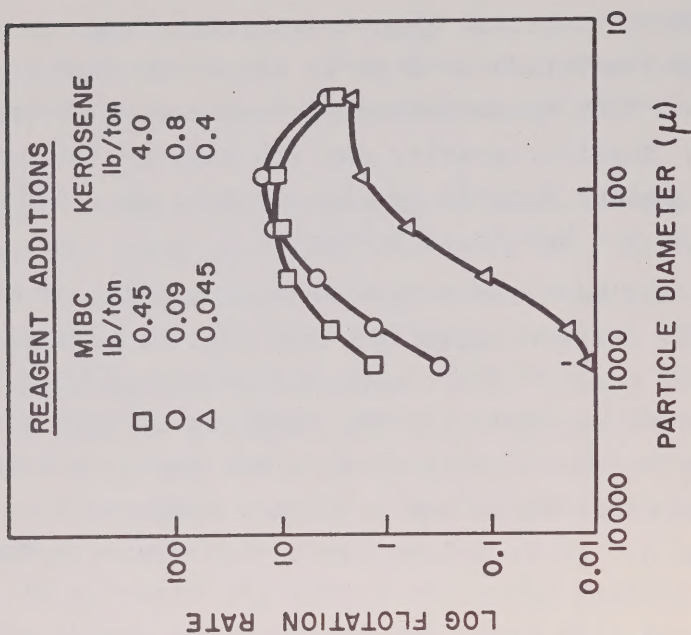


Fig. 3. EFFECT OF REAGENT ADDITIONS ON THE FLOTATION RATE OF COAL

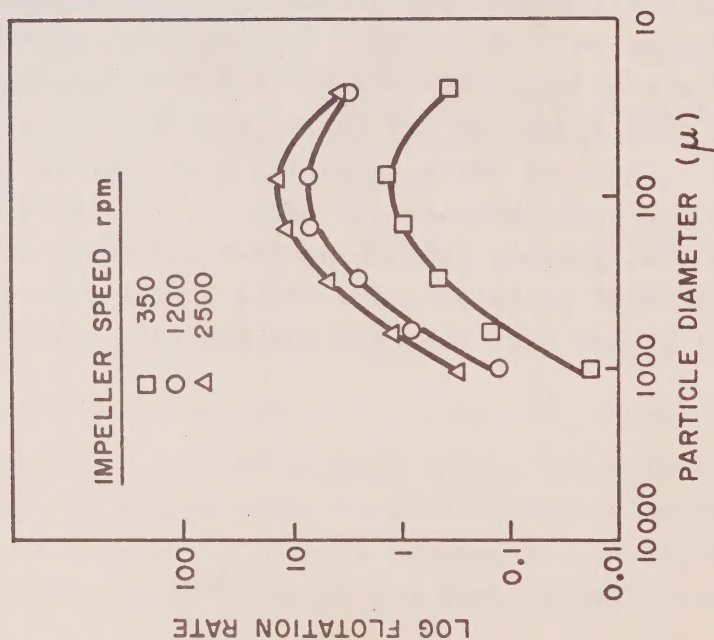


Fig. 2. EFFECT OF IMPELLER SPEED ON THE FLOTATION RATE OF COAL

A recent study (85) of froth flotation for the separation of pyrite from coal has shown that careful control of the variables that affect the process is important. These variables include collector concentration, air flow-rate, concentration of inorganic reagents, and size distribution in the feed, with the concentration of the collector (MIBC) being particularly important. In a single-stage flotation separation, some pyrite was found to report with the coal and this was separated in a second flotation step in which the froth product was re-pulped and the pyrite floated in the presence of a coal depressant. The clean coal was recovered as the underflow from the second flotation stage. Reductions in the ash and the pyritic sulphur content of the cleaned coal were of the order of 70 per cent.

4.1.4 Spherical Agglomeration.

Spherical agglomeration is a process for the selective removal of particles from a liquid suspension by the addition of a second immiscible liquid which has a greater affinity for the solid phase than the first liquid (86). Under conditions of high-speed agitation, agglomerates of the solid phase are formed in a few minutes, which can be removed from the bulk liquid phase by screening or filtration. The method has a high efficiency for the recovery of very finely divided materials (minus 200-mesh) and has been used as an alternative technique to vacuum filtration and thermal drying for the removal of moisture from fine coals (39,43,87,88). It has also been used for the preparation of low-moisture, uniform-sized coal pellets which have acceptable characteristics for charging to coke ovens (43).

Coals are naturally hydrophobic and agglomerate readily with almost any kind of oil. As little as three weight per cent of a bridging oil is sufficient (39) to reduce the moisture content of micro-aggregates by about one-half of that of un-oiled coal (Table 11).

TABLE 11

AGGLOMERATION AND DE-WATERING OF A
28 x 0-MESH WESTERN CANADA COAL

Diesel Oil Added (wt % on dry basis)	Water in Filter Cake (%)	Ash in Filter Cake, Dry Basis (%)	Recovery of Combustibles (%)
0.0	23-24	12.5	-
3.1	13-15	11.8	>99
9.3	10-12	9.8	>99
15.5	9-11	9.6	>99

Larger agglomerates (1/4 inch to 1/2 inch), of still lower moisture content, may be obtained by using larger quantities of oil; however, cost considerations are important in governing the total amount of oil that can be economically employed in this process (39,43).

Although many bridging oils may be used for the agglomeration of fine coals, the best selectivity for the separation of fine coals from ash minerals is obtained with light oils (89). Some recovery data with various oils are given in Table 12 where it will be noted that heavy oils are relatively unselective (89).

TABLE 12

INFLUENCE OF VARIOUS OILS ON THE BENEFICIATION OF COAL

Collecting Oil	Temperature (°C)	Percentage Ash in Product	Percentage Recovery of Combustibles
Fuel Oil	21	7.2	97
Kerosene	21	5.2	83
Kerosene	90	5.5	-
Varsol	21	2.7	91
50% Kerosene + 50% Bunker C oil	21 90	10.6 14.0	- 92
Light Coal Tar	21	19.0	90
Light Coal Tar	90	15.7	90

The coal (Avon Coal Co., St. John, New Brunswick) employed in these tests contained 21.1 per cent ash and 6.3 per cent sulphur, and was a minus 1-mm fraction (51.9% < -22 microns) from a wash-plant slurry normally recovered by flotation.

Pyrite tends to be hydrophobic and to agglomerate with coal in spherical agglomeration. To separate pyrite from coal it is therefore necessary to use surface conditioning agents (depressants) to render the pyrite surface hydrophillic and to keep it in the aqueous phase. With chemical depressants it has been found possible to remove about 50 per cent of the pyritic sulphur from coal, and initial tests show that improved depression (~ 90%) of the pyrite is obtained if the coal is ground in the presence of the bacterium *Ferrobacillus ferrooxidans* (39). This bacterium selectively oxidizes the pyrite to the sulphate form, rendering

its surface hydrophillic.

In general, spherical agglomeration appears to be an effective technique for the de-watering of very fine coals. The method may be useful for the recovery of coal used in long-distance pipe-line transportation where a significant fraction of the coal is less than 325 mesh. Techniques now under development also have applications to the removal of pyritic sulphur from coal; the main problem, however, is the cost of the separation in terms of fine grinding and oil consumption.

4.2 DRY SEPARATION METHODS

The beneficiation of coal by 'air washing' is widely practised in the coal industry (90). The method depends on the difference in specific gravity between coal and its mineral impurities and is usually employed to clean feed-coal in the size range between 1/4 inch and 48 mesh. It is an economical technique for the removal of coarse mineral impurities (including pyrite) but is unsuitable for the removal of finely disseminated pyrite or organic sulphur. The removal of small pyrite particles from coal has been studied on a laboratory scale by three dry techniques based upon centrifugal, electrostatic, and magnetic separation methods.

Centrifugal separation has been studied by Abel et al. (91). They used a centrifugal separator in which finely divided coal was fed onto a spinning spreader disc. The lighter particles were ejected into a rising stream of air and collected as a cleaned product in an annular space between the inner and outer walls of the separator. Particles which were too heavy to become entrained in the air stream fell into a tailings cone and were collected as the heavy-product fraction. This fraction was enriched in pyrite and could be subjected to further cleaning steps. - Because centrifugal separation classifies the sample into two fractions, depending on the mass of the individual particles, a closely sized feed was chosen. It was found that as the particle size in the

feed was decreased the amount of pyrite in the reject fraction increased, e.g., in changing size increments from a 68 to 80-mesh feed to a 270 to 400-mesh feed, the amount of pyrite in the reject increased from 17.2 per cent to 58.8 per cent (Table 13).

TABLE 13

THE DRY REMOVAL OF PYRITE FROM CLOSELY
SIZED FRACTIONS OF PITTSBURG COAL BY
CENTRIFUGAL SEPARATION

Mesh Size	Portion of Grind (%)	Percentage of Total Pyritic Sulphur in 10% Heavy Fraction
60-80	2.4	17.2
80-100	3.1	14.3
100-150	10.2	17.5
150-200	12.7	20.4
200-270	10.4	30.1
270-400	12.0	58.8
400-0	49.2	3.6

The degree of separation and the mass of the particles collected in centrifugal separation can be modified to some extent by controlling the velocity of air in the separator. Thus at low air velocities only the fine particles are removed. The time of grinding is also an important variable in this process. Pyrite requires a much longer milling time than coal for fine grinding and the milling times prior to separation are optimized to limit the grinding of coarse pyrite particles, and thus to enhance the mass difference between the resultant pyrite and coal particles.

The electrostatic separation of powdered solids depends on differences between the electrical characteristics of the solids and, for non-metals, is dependent on their solid-state properties, the temperature of separation, and the metal used to provide electrical contact with the powder (92). Because of variations in the properties of different coals, it has been suggested that the conditions for electrostatic separation (e.g., drum speed and type of electrodes) should be selected specifically for each type of coal (93). Normally pyrite is more conductive than coal and is released from the rotor of the separator (94). Some laboratory measurements have been made on the application of a drum-type separator (18 to 30 kV applied potential) for the removal of pyrite from a Pittsburgh coal (91). As with centrifugal separation, the best results in a single-pass unit are obtained if closely sized fractions are used (91,93,95) and if the pyrite is maintained as large as possible by control of the grinding time. The stage grinding of coal, together with a combined centrifugal-electrostatic separation system, has been described (91) in which 33 to 55 per cent of the pyritic sulphur was removed from a Pittsburgh coal in rejects of 10 to 15 per cent. Inculet et al. (96) have studied the charge developed on various coal components in a fluidized bed, while subjected to an electrical field. Finely divided coal (New Langan Mine, Cape Breton) was used and allowed to fall from the fluidized bed between two vertical electrodes in an electrostatic separation tower. Insulated trays at the base of the tower were used to collect the coal into fractions (depending on their induced charge) and to allow the measurement of the electrical charge acquired by the coal. Preliminary results indicate that the different components in the coal developed distinct electrical charges which may be used for separation purposes.

Small-scale laboratory tests have shown that it is possible to separate pyrite from coal in a high-intensity magnetic separator (97,98). However, it has been suggested (99) that the

difference between their magnetic susceptibilities (coal, -4×10^{-7} cgs units; pyrite, 3×10^{-7} cgs units) is too small for efficient separation to be made on a large scale, and that the susceptibility of the magnetic fraction must be raised to at least 3×10^{-6} cgs units. The 'apparent' magnetic susceptibility of pyrite could be increased by converting a small part of it into a lower sulphide, or into an oxide, both of which have large magnetic susceptibilities at room temperature (Table 14). The pre-treatment of coal with super-heated steam (150 to 300°C) has been reported (100-102) to enhance the magnetic separation of pyrite through the formation of films of magnetite, hematite, and pyrrhotite on the surface of the pyrite. However, other workers have found that such thermal treatment gives either a poor quality product or no beneficiation, and that a superior quality coal could be obtained by magnetic separation of untreated coal (97-99, 103). Ergun and Bean (99) claim that to achieve adequate conversion of pyrite to pyrrhotite, temperatures in excess of 400 to 500°C are required. Russian workers (104) have found that heating lignite (particle size < 1 mm; sulphur content, 7.55%) to 600°C, followed by magnetic separation of the 'magnetically enhanced' pyrite in a roller-type magnetic separator at 9,000 Oe, gave a 79.8 per cent yield of a concentrate containing only 2.8 per cent sulphur.

Ergun and Bean (99) have proposed a novel method for the selective conversion of part of the pyrite in coal to a more magnetic form by dielectric heating in the Mhz to Ghz frequency range. Due to the large difference between the imaginary dielectric constants of coal and pyrite (at 20 Mhz; pyrite, 5; coal, 0.015) pyrite will be selectively heated in the coal matrix. The coal need not be finely ground prior to dielectric heating, although grinding to 200 to 400 mesh is noted in a recent patent (105). Preliminary measurements showed that pyrite could be heated to above 500°C in the presence of coal without a significant rise in the temperature of the coal, and that some magnetic beneficiation occurred. A

TABLE 14
THE MAGNETIC SUSCEPTIBILITIES OF SOME IRON COMPOUNDS AND
THE 'APPARENT' SUSCEPTIBILITY OF PYRITE IF ONE PER CENT
OF THE COMPOUND WERE PRESENT IN THE PYRITE

Iron Compound	Magnetic Susceptibility Per Gram of Compound (cgs units x 10^6)	'Apparent' Magnetic Susceptibility per Gram of Pyrite if 1% Converted Into Iron Compound (cgs units 10^6)
Monoclinic Pyrrhotite, $\text{FeS}_{1.14}$	2,800	22
Magnetite, Fe_3O_4	15,600	101
Gamma Hematite, $\gamma\text{Fe}_2\text{O}_3$	15,600	104
Alpha Hematite, $\alpha\text{Fe}_2\text{O}_3$	20.6	0.4
Pyrite, FeS_2	0.3	0.3

similar high-frequency heating technique has been used by Tait and Andreeva (104) for the removal of pyrite from lignite. They obtained a significant reduction in the sulphur content of the lignite (7.55% to 2.90%) with a yield of 87.6 per cent.

Work at the U.S. Bureau of Mines has also been reported (106) in which the magnetic susceptibility of pyrite was increased by grinding coal in mills equipped with ferromagnetic grinding elements. It appears that the increase in magnetic susceptibility resulted from some of the grinding medium being abraded into the harder pyrite surface and this type of approach could provide a physical method to increase the magnetic susceptibility of pyrite.

CHEMICAL SEPARATION METHODS

Recently a number of chemical processes have been proposed for the selective removal of pyritic and/or organic sulphur from coal. These methods have the potential advantage of giving almost complete removal of inorganic sulphur and/or significant reduction of the organic sulphur content of coal; however, they are currently at the laboratory or pilot-plant stage of development and have not achieved commercial realization.

5.1 SOLVENT-REFINED COAL

Solvent-refined coal is a reconstituted coal which is free of water and which has a very low ash content (107-112). A process for its preparation has been under development since 1962 (111) by the Pittsburgh and Midway Coal Mining Company, under contract from the Office of Coal Research of the United States Department of the Interior. The method may be used to treat almost any kind of coal, with the possible exception of anthracite (109), and yields a product with an enhanced heating value over the initial feed coal. Solvent-refined coal has a uniform heating value of about 16,000 Btu/lb regardless of the coal from which it was prepared (112). A schematic of the Pittsburgh and Midway process is given in Figure 4. The coal is

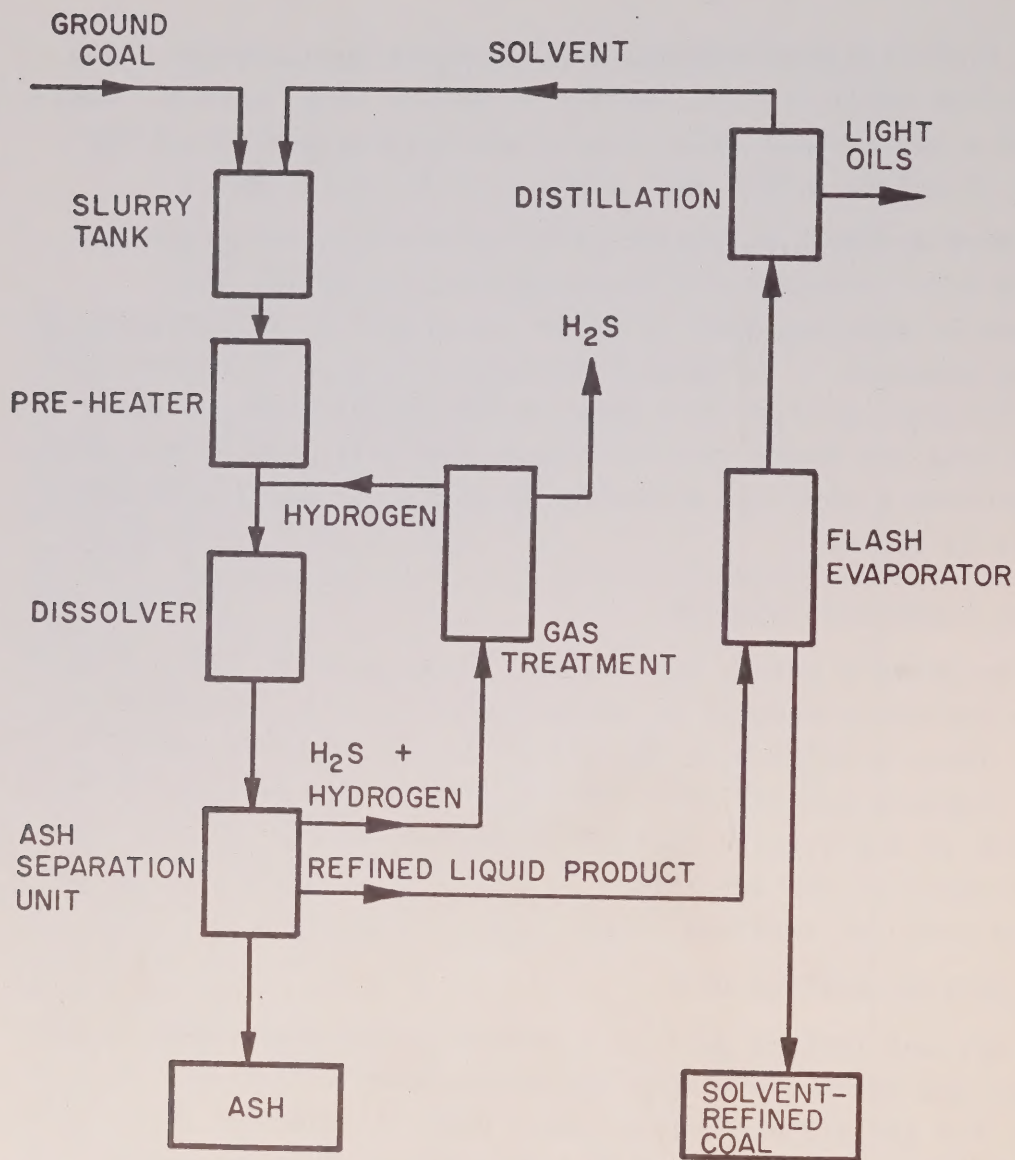


Fig. 4. SCHEMATIC OF THE PITTSBURGH AND MIDWAY SOLVENT-REFINED-COAL PROCESS

first ground to minus 200 mesh and is then slurried with a solvent oil (boiling range, 500 to 800°F). The slurry is then heated under pressure in a pre-heater and passed to a dissolver which operates at about 800°F and 1,000 psi. Hydrogen, which is added to the slurry prior to the pre-heating stage to prevent polymerization of the dissolved coal, also reduces some of the organically bound sulphur to hydrogen sulphide from which elemental sulphur may be recovered in an ancillary gas-treatment step. The amount of hydrogen consumed is about one to two per cent by weight of coal (112). A catalyst is not used during hydrogenation, although there is experimental evidence that inorganic material in the coal acts as an 'internal' catalyst (113). After the coal has dissolved, the insoluble matter is separated by filtration. The solvent is then recovered by flash evaporation and is re-cycled to the slurry tank. Additional solvent make-up is not required because solvent oil is released from the coal during processing. When balanced solvent operation is maintained (i.e. when the process is self-sustaining in recycle solvent alone), solvent-refined coal has viscosity characteristics that allow it to be handled as a hot liquid; a property which may provide a market for solvent-refined coal as an alternative fuel to diesel oil in locomotives (109). The hot, liquid residue from the solvent filtration step is discharged and cooled to yield solvent-refined coal which contains about 90 per cent of the carbon in the original coal feed. Solvent-refined coal melts at about 130°C and resembles pitch in physical appearance. It is a brittle material that may be readily crushed for use in pulverized coal boilers. The ash from the ash-separation stage contains about five to eight per cent sulphur and significant quantities (35 to 55 per cent) of carbon and may be burned to recover its heating value. The off-gases, relatively rich in sulphur dioxide, may be combined with hydrogen sulphide from the coal dissolution stage to give sulphur by the Claus reaction (114).

In general, the solvent refining process removes all the ash and pyritic sulphur from coal. The reduction in the organic

sulphur content is over 60 per cent. Thus for feed coal containing three per cent sulphur equally divided between the organic and inorganic forms, the solvent-refined-coal product would have a sulphur content of less than 0.6%. For coals containing more than fifty per cent sulphur in the inorganic form, the percentage sulphur reduction would be even greater.

The acceptance of solvent-refined coal is strongly influenced by its cost. A recent estimate (112) gives an on-site price of 40 to 50 cents/million Btu, the price-range depending on the sale of by-product light oil and sulphur. In a number of locations this price is similar to that of low-sulphur oil and coal and may be compared to an estimated cost (115) of up to 27 cents/million Btu for the installation and operation of flue-gas desulphurization equipment.

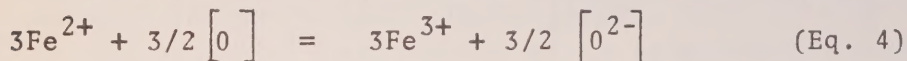
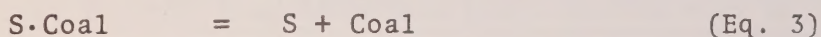
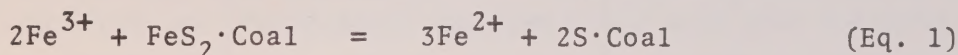
An economic assessment has been made of the use of solvent-refined coal in large thermal power stations and the results compared to the cost of using untreated coal, with gas cleaning equipment for the removal of particulate matter and sulphur dioxide (116). With a combustion unit designed specifically for solvent-refined coal, savings accrue in the investment and operating costs for fly-ash removal and disposal, and in the reduced size of the combustion unit. The use of an ash-free, low-sulphur fuel also provides unequivocal pollution control because no unusual effluent emissions can occur through the breakdown of flue-gas treatment equipment, and it is especially useful for power plants that are too small to justify the installation of equipment for the removal of sulphur dioxide from flue gases. Freight costs are also less with solvent-refined coal because its heat content per unit weight is greater than that of untreated coal.

It has been announced recently (117) that a fifty-ton-per-day pilot plant is to be built near Tacoma, Washington to produce solvent-refined coal by the Pittsburgh and Midway process. The plant is scheduled for completion in late 1973 and will test the

scale-up of the process and also produce sufficient product for large-scale testing of its combustion characteristics.

5.2 FERRIC-ION LEACHING

The removal of pyritic sulphur from coal by the oxidation of pyrite with ferric-ion solutions is undergoing bench-scale development by TRW Systems, California (118-122). The basic steps in the method are shown in Equations 1 to 4, and involve the formation of elemental sulphur (Equation 1) and ferrous sulphate (Equation 2) from the pyrite, the recovery of sulphur from the pores of the coal (Equation 3), and the regeneration of ferric ions by air oxidation (Equation 4).



Although various reagents may be used to oxidize pyrite (47,123), a solution of ferric ions has the unique advantage that separation of the oxidizing agent from the iron extracted from the pyrite is not necessary, i.e. "iron is used to remove iron" (120). Kinetic measurements have been made of the rate of ferric-ion oxidation of samples of marcasite and pyrite, obtained from a coal-washing plant in New South Wales (124). The studies were conducted in a nitrogen atmosphere and indicated that both minerals were oxidized at about the same rate and that ferric chloride and ferric sulphate were equally effective as oxidizing agents. The activation energy for the reaction between iron disulphide and ferric ions was 20.5 kcal/mole.

The experimental procedure adopted by TRW Systems for the removal of pyrite from coal by ferric-ion leaching involves treating the ground coal at about 100°C with a one-molar solution of ferric chloride or ferric sulphate. Increasing the leaching

time has been found to be not as effective in pyritic sulphur removal as renewing the leach solution, and the experimental data reported so far involve successive batch-type leaching with fresh solutions. Six one-hour leaches with fresh one-molar ferric chloride solutions were shown (119) to remove almost all the pyrite from four representative coals from the eastern United States (Table 15).

TABLE 15
THE REMOVAL OF PYRITIC SULPHUR FROM COAL BY
SIX ONE-HOUR LEACHES WITH ONE-MOLAR FeCl_3 SOLUTIONS

Coal	Pyritic Sulphur Analysis (%)		Pyritic Sulphur Removal (%)
	Initial	Final	
Lower Kittanning	3.58	0.06	98
Pittsburg	1.20	0.09	93
Illinois No. 5	1.57	0.10	94
Herrin No. 6	1.65	0.05	97

About sixty per cent of the sulphur in the pyrite was found to be oxidized to the sulphate form (Equation 2). The amount of pyrite removed is dependent only to a limited extent on the coal top-size from minus 1/4-inch to minus 200-mesh (119), inferring that very fine grinding is not required for the successful application of this process. Following leaching the aqueous solution is separated from the coal which is then washed to remove residual solution. Elemental sulphur may be recovered from the coal matrix either by extraction with a suitable solvent (toluene or kerosene) or by vacuum vaporization. Iron oxide is also a by-product of this method and a schematic of a process flow-chart is given in

Figure 5.

A preliminary economic assessment of the cost of pyritic sulphur removal from coal by ferric-ion leaching (120), for a plant treating 2,400 tons of coal per day, gives an estimated processing charge of \$1.95 per ton of coal ($\sim$ 8 cents per million Btu).

5.3 ORGANIC-SOLVENT LEACHING

A study has been made of the extraction of organic sulphur from four coals (Illinois No. 6, Indiana No. 5, Pittsburg, and Bevier) by a variety of organic solvents and by aqueous solutions of inorganic acids and bases (125). The extractions were usually conducted at the boiling point of the solvent and at atmospheric pressure. It was found that the inorganic acid and alkaline solutions removed small amounts of organic sulphur from some of the coals but were totally ineffective with others. Organic bases and neutral organic compounds were also ineffective in sulphur removal. However, weak organic acids, particularly nitrobenzene and phenols, removed from 45 to 80 per cent of the organic sulphur, depending on the process conditions and the type coal. p-Cresol was suggested as the most attractive phenol in view of its cost, availability, and thermal stability. The nitrogen content of coal was also reduced by leaching with p-cresol. This reduction in nitrogen content is an advantage because the amount of NO_x in combustion gases is related to the nitrogen content of the coal (126). A disadvantage with p-cresol for solvent leaching is that grinding of the coal to minus 200 mesh is required to obtain a significant reduction in its organic sulphur content (based on a one-hour extraction).

The mechanism of the removal of organic sulphur from coal by organic-solvent leaching is suggested (125) to involve the selective depolymerization and dissolution of the organic sulphur compounds from the coal structure, without significantly altering the remainder of the coal matrix. The economics of sulphur

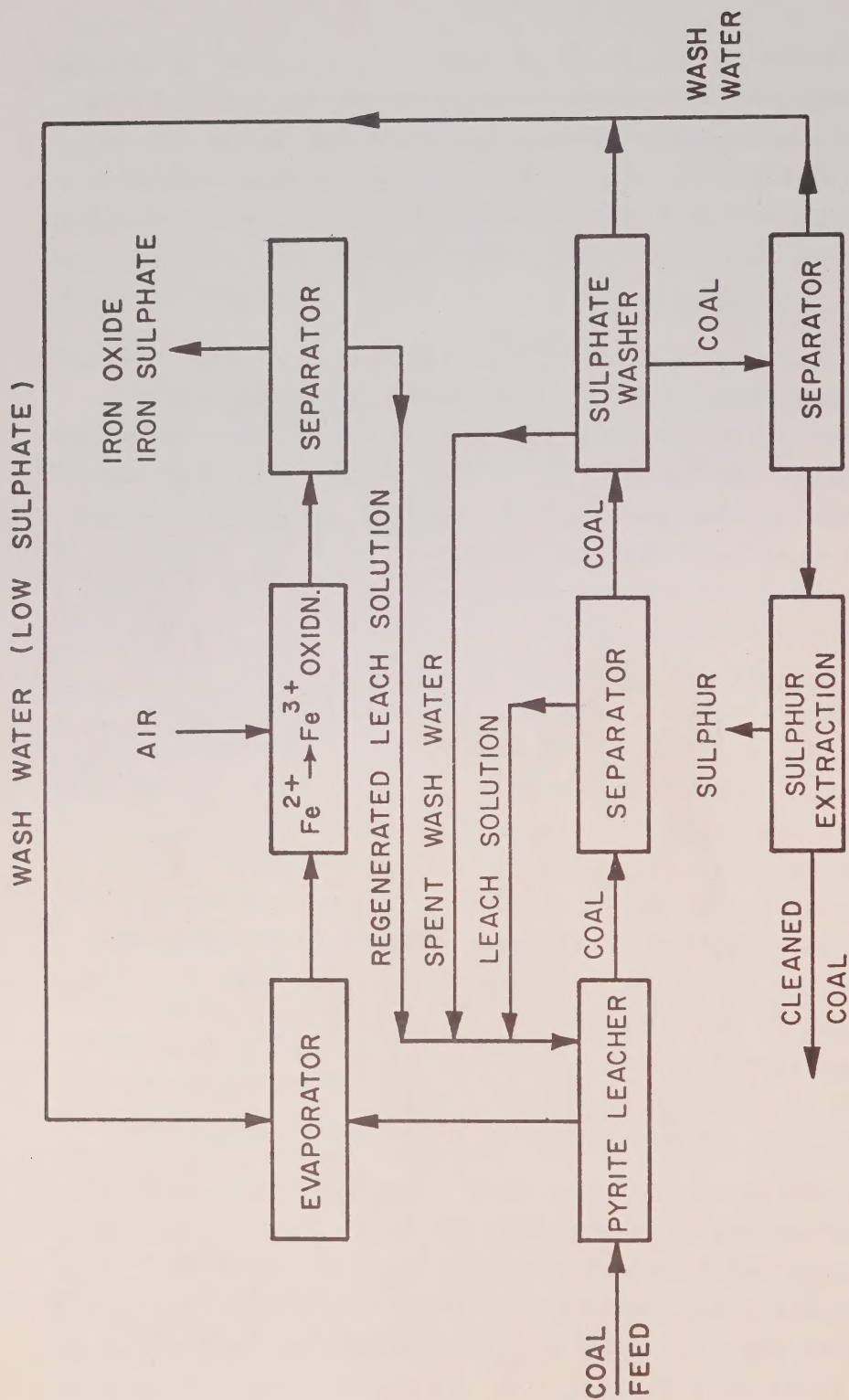


Fig. 5. PYRITIC SULPHUR REMOVAL FROM COAL BY FERRIC ION LEACHING

removal by this method are very dependent on the amount of solvent lost during re-cycling and on the ability of the solvent to have a high carrying-capacity for sulphur compounds. A preliminary estimate gives the cost of organic-solvent sulphur-removal at between \$1.00 to \$1.50 per ton of coal. A schematic of one possible process is given in Figure 6.

5.4 ALKALINE LEACHING

Pyritic sulphur may be completely removed from coal by reaction with a 1:1 mixture of sodium hydroxide and potassium hydroxide at elevated temperatures (127,128). The pyrite is decomposed to form sulphides which dissolve in the alkaline melt. The reaction is rapid above 250°C and is essentially complete in ten to fifteen minutes. Longer reaction times and higher temperatures also lead to the removal of some of the organic sulphur in the coal. At temperatures below about 300°C the coal should be ground to at least minus 40 mesh. However coarser coal can be used above 300°C, because at these temperatures the coal becomes 'plastic' which facilitates the reaction between pyrite and the caustic melt. High-volatile bituminous coals (Pittsburg and Illinois) can be readily treated by this method giving recoveries of 90 to 95 per cent, but a low-rank coal (Wyoming) was extensively decomposed by the molten alkali and only 52 per cent remained after 30 minutes treatment at 200°C.

The treatment of a bituminous coal (Illinois No. 6) with an aqueous solution of ten per cent sodium hydroxide in a stirred autoclave for two hours at 250°C also removed essentially all of the pyritic, but none of the organic sulphur, from the coal (129). Acidification of the coal with dilute hydrochloric acid after the alkaline treatment also significantly reduced its ash content from 9.8 to 0.7 per cent. This reduction in ash content was thought to arise from the formation of sodium aluminum silicates from the clay minerals during the alkaline treatment. These silicates are insoluble in the alkaline solution but dissolve on treatment with strong acids.

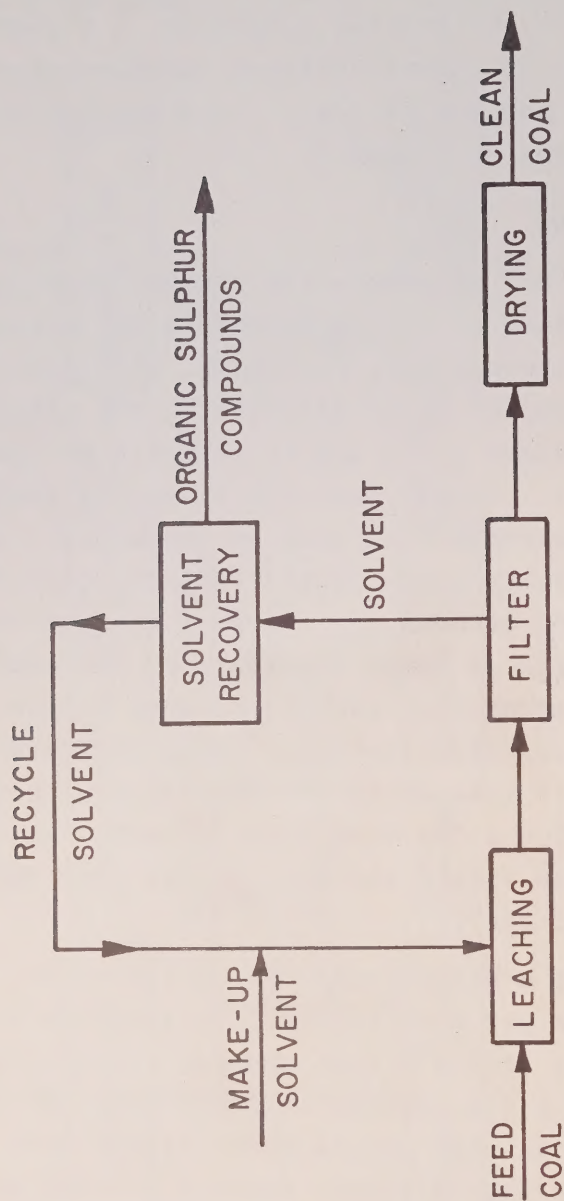


Fig. 6. ORGANIC SULPHUR REMOVAL FROM COAL

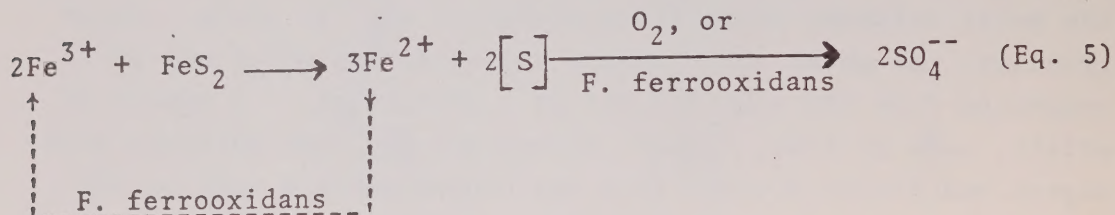
6. OTHER METHODS

Winkler (130) has made a feasibility study of the removal of organic sulphur from a coal-oil mixture by attrition grinding of the mixture in the presence of a finely divided metal powder. The metal powder acts as a scavenger for organic sulphur, forming the metal sulphide which is insoluble in the oil phase. After grinding, the metal sulphide and any unreacted metal may be separated from the coal and oil in a centrifuge. A number of metals, such as iron, copper, nickel, and tin, are suitable scavengers and finely divided iron was chosen in this work on the basis of cost. It was found that grinding in a steel ball mill for five minutes at 250°C gave a reduction of 50 per cent in the sulphur content of the coal-oil mixture. For the best removal of organic sulphur from coal the use of predominately aromatic oils was recommended.

The removal of pyritic sulphur from coal by low-temperature (350 to 450°C) air oxidation has been described by Sinha and Walker (131). Seven coals were studied which contained from three to seven per cent total sulphur and in which the sulphur was approximately equally distributed between the organic and the inorganic forms. It was found that temperature was the most important factor in desulphurization and that for some coals over 90 per cent of the pyritic sulphur was removed by heating for ten minutes at 450°C. The efficiency of sulphur removal was controlled by the diffusion of air into the coal-pyrite matrix. The calorific value and the volatile content of the coal were somewhat reduced as a result of desulphurization by this method.

It has been found that certain acidophillic bacteria, e.g., *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans*, have the ability to reduce the pyrite concentration of coal (132,133). The mechanism of this bacterial action is not fully understood and it has been suggested (134) that two concurrent processes may be involved; 1) the direct biological oxidation of pyrite by the bacteria and 2) the oxidation of pyrite by ferric ions, followed

by bacterial oxidation of the product ferrous ions to regenerate the primary oxidant (Fe^{3+}) for further oxidation of the pyrite. In this mechanism (133) the *Ferrobacillus ferrooxidans* does not attack the pyrite directly (Equation 5), but is responsible for the aerobic oxidation of ferrous ions to ferric ions.



Russian workers (132) found that *Thiobacillus ferrooxidans* removed 23 to 27 per cent of the pyrite from a Donets basin coal in thirty days and the same bacterium is also used for the recovery of metals from sulphide ores (135). In a laboratory study of the effect of *Ferrobacillus ferrooxidans* on bituminous, sub-bituminous, and lignite coals, Silverman et al. (133) found in some cases that over 80 per cent of the pyrite was removed from the coal in four days. They also found that the relative order of pyritic sulphur removal from the coals was bituminous > sub-bituminous > lignite and that bacterial action was most effective for small coal particles (minus 325 mesh). The large-scale application of this approach to the removal of pyrite from coal would involve difficulties in the preparation and handling of very small particles, and in the disposal of pyrite oxidation products (sulphuric acid and iron salts) without creating a water pollution problem.

A small-scale laboratory study has been made (85,136) of the electrophoretic separation of coal from its mineral impurities. Although a reduction in the pyrite content of the coal was obtained, the method was considered impractical for commercial coal preparation.

7. SUMMARY

Environmental constraints on the amount of sulphur dioxide that may be released to the atmosphere from the combustion of coal have focussed attention on methods for the removal of sulphur from coal before combustion. Much of this work has been concerned with the removal of pyritic sulphur using physical cleaning methods. For such methods, the theoretical upper limit on the amount of sulphur that may be removed is given by the organic sulphur content of the coal. However, in practice, the total amount of sulphur that may be removed from a given coal is dependent not only on the distribution of sulphur between its organic and inorganic forms, but also on the amount of pyritic sulphur which may be liberated from the coal by grinding. Generally, to achieve significant pyritic sulphur reductions it is necessary to use fine grinding and to perform physical separations at specific gravities close to that of coal. By this approach large reductions in the pyritic sulphur content of coal may be achieved through the use of cleaning methods that are either well-established or currently under development. However, good efficiency for pyritic sulphur removal is usually accomplished with low yields of clean coal and the choice of a method most suitable for a given coal is dependent on the proposed application of the product and on various factors inherent in the type of coal itself, and is ultimately governed by economic considerations.

The complete removal of pyritic sulphur from coal may be achieved either by the dissolution of the coal in an organic solvent, followed by filtration to remove inorganic materials and the subsequent re-constitution of the hydrocarbon phase, or by methods based upon the selective chemical leaching of pyrite from the coal matrix. These methods are currently in the development stage and only the solvent-refined-coal process is being scaled-up to the pilot-plant level. This latter method has the unique advantage of removing virtually all inorganic material from coal, and also of giving a significant reduction in its organic sulphur

content. The large-scale application of this process to coal cleaning is dependent on the results of the current pilot-plant study. However, assuming that the economic and engineering factors are favourable, the industrial utilization will still be some years away.

At present only coals containing 1 to 1.5 per cent sulphur can be economically desulphurized by physical techniques to levels necessary to meet emission standards of the type proposed in the United States. The main benefit of these cleaning methods for high-sulphur coals is as a primary upgrading step, which allows the partially desulphurized coals to be used in conjunction with relatively low-efficiency treatment methods for the removal of sulphur dioxide from flue gases.

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